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# Longitudinal and bulk viscosities of expanded rubidium

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## Abstract

First three non-vanishing sum rules for the bulk and longitudinal stress auto-correlation functions have been evaluated for liquid Rb at six thermodynamic states along the liquid–vapour coexistence curve. The Mori memory function formalism and the frequency sum rules have been used to calculate bulk and longitudinal viscosities. The results thus obtained for the ratio of bulk viscosity to shear viscosity have been compared with experimental and other theoretical predictions wherever available. The values of the bulk viscosity have been found to be more than the corresponding values of the shear viscosity for all six thermodynamic states investigated here.

## 1. Introduction

The bulk viscosity can be considered as a measure of the resistance offered by a medium subjected to the forces of compression or expansion. In fact, it plays an important role in understanding the intermolecular forces of attraction and also the acoustic phenomena at a microscopic level. In addition, bulk viscosity plays an important role in the study of the dynamical structure factor, a quantity which is directly measurable in neutron diffraction experiments. Despite its immense importance, the bulk viscosity of a fluid is the least studied among all the atomic transport coefficients, like diffusion, shear viscosity and thermal conductivity. One of the unavoidable reasons for this is that one carries out experimental measurements of bulk viscosity only by indirect methods. Nevertheless, there exist [1–4] some estimates for the bulk viscosity of various liquids, which encourage one to study this quantity using a microscopic approach.

Microscopically, one can study bulk viscosity by the Green–Kubo method which expresses it [5] as the time integral of the bulk stress–time auto-correlation function. The bulk stress auto-correlation (BSAC) function can be calculated by using Mori’s memory function approach [5–7] coupled with its sum rules. We have derived expressions [7] for the sum rules of the BSAC function which were further used to study bulk viscosity in a Lennard-Jones (LJ) fluid. Another equivalent approach to calculating bulk viscosity is through the evaluation of longitudinal and shear viscosity by exploiting the relation  $\eta_B = \eta_l - 4/3\eta_s$ , where  $\eta_B$ ,  $\eta_l$  and  $\eta_s$  are, respectively, the bulk viscosity, longitudinal viscosity and shear viscosity. The

longitudinal viscosity and shear viscosity can be estimated through the knowledge of the time development of longitudinal and transverse stress auto-correlation functions. Sum rules for these auto-correlation functions have also been derived [7, 8] and have been used to study the bulk viscosity of LJ fluids. It was found that both methods have provided a good description of the bulk viscosity coefficient, as has been judged by comparing our results with those obtained from computer simulations [9, 10]. In fluids like Ar, it is known [1, 9] that the ratio of bulk viscosity to shear viscosity is always less than 1. However, in the case of liquid metals, this ratio has been found to be greater than one. For example, in the case of Rb, this ratio near the melting point was experimentally found [11] to be around 3.73. Recently, Okumura and Yonezawa [12] derived a new formula for the bulk viscosity in terms of the pair potential and derivatives of the pair distribution function,  $g(r)$ . They have also studied [13] the behaviour of a modelled liquid metal for which the interatomic potential is density-dependent and it is found that the bulk viscosity is sensitive to the shape of the potential. Derivatives of  $g(r)$  w.r.t. density and  $r$  appears in their expression. Though these derivatives are related to triplet correlation function, it does not provide explicit information about the role played by the triplet correlation function in determining the bulk viscosity. Therefore, it is also of interest to study the behaviour of the viscosities of liquid metals at different densities and temperatures using the density-dependent interatomic potential and to extract information about the role played by three-particle correlation.

In the present work, we study the bulk viscosity of the expanded Rb along liquid–vapour co-existence curve at six thermodynamic states. We have employed a pseudo-potential and corresponding pair distribution function to [14] evaluate at first three non-vanishing sum rules of the bulk and longitudinal stress auto-correlation functions (LSAC). Bulk and longitudinal viscosities have been estimated by using values of the sum rules and Mori’s memory function formalism. The results obtained have been compared with corresponding values of shear viscosity and other estimates wherever available. It has been found that the bulk viscosity calculated from the BSAC function is consistent with the values obtained from the knowledge of longitudinal and shear viscosities. It is also found that the ratio of bulk viscosity to shear viscosity is greater than 1 for all the thermodynamic states investigated here, which is consistent with earlier predictions [15] and the experimental result [11] wherever available. The effect of three-body correlation has also been studied in predicting bulk and longitudinal viscosities. It has been found that three-body correlations play a very important role in estimating the viscosities of metals.

The layout of the paper is as follows. In section 2 we present the theory involved. Section 3 contains the results and discussion. The summary and conclusion is brought out in section 4.

## 2. Theory

The theoretical approach, which is more frequently used for dense fluids, is through the Green–Kubo method. The Green–Kubo formula for the calculation of longitudinal viscosity is given as

$$\eta_l = \frac{1}{Vk_B T} \int_0^\infty dt S^l(t). \quad (1)$$

In the above equation,  $S^l(t)$  is the LSAC function defined [5] as

$$S^l(t) = \frac{1}{3} \langle J^{aa}(t) J^{aa}(0) \rangle, \quad (2)$$

with

$$J^{ab} = \sum_{j=1}^N \left( \frac{p_{ja} p_{jb}}{m} + r_{ja} F_{jb} \right) - \delta_{ab} V \left( P + \frac{dP}{dE} (E - \bar{E}) \right), \quad (3)$$

where  $a$  and  $b$  run over  $x, y$  and  $z$ . Also  $p_{ja}, r_{ja}$  and  $F_{ja}$  are the  $a$ th component of velocity, position and force, respectively, of the  $j$ th particle. The angular brackets represent the canonical ensemble average.  $P, V, k_B, T$  and  $m$  are the average pressure, volume, Boltzmann constant, temperature and mass, respectively. The first two terms in equation (3) represent the momentum current due to kinetic and potential contributions to viscosity, whereas the last term is suitable for a NVT ensemble. The inclusion of the last term is essential so as to get the appropriate density dependence even for an ideal gas. Expressions for  $\bar{E}$  and  $PV$  in terms of the pair potential,  $u(r)$ , and pair distribution function,  $g(r)$ , are given as

$$\bar{E} = \frac{3}{2}Nk_B T + 2\pi n \int_0^\infty r^2 g(r)u(r) dr, \tag{4}$$

and

$$PV = Nk_B T - \frac{2\pi n}{3} \int_0^\infty dr r^3 g(r) \frac{du(r)}{dr}. \tag{5}$$

The second Green–Kubo relation, which relates the bulk viscosity,  $\eta_B$ , directly to the so-called BSAC function,  $S^B(t)$ , is given [5] by

$$\eta_B = \frac{1}{Vk_B T} \int_0^\infty dt S^B(t), \tag{6}$$

where

$$S^B(t) = \frac{1}{9} \sum_a \sum_b \langle J^{aa}(t) J^{bb}(0) \rangle. \tag{7}$$

The exact calculation of  $S^{B/l}(t)$  is a difficult task for realistic fluids as it involves the correlation of two dynamical variables at two different times. Therefore, we use Mori’s equation of motion [6] to calculate  $S^{B/l}(t)$ . Mori’s equation is given as

$$\frac{dS(t)}{dt} = - \int_0^t M_1(t - \tau) S(\tau) d\tau, \tag{8}$$

where  $M_1(t)$  is the first-order memory function which, at  $t = 0$ , is related to the sum rules of  $S(t)$ . We have suppressed the superscript  $l$  or  $B$  as the procedures followed for the evaluation of  $S^B(t)$  and  $S^l(t)$  are the same. The frequency sum rules of  $S(t)$  are given by the short time expansion coefficient defined as

$$S(t) = S_0 - S_2 \frac{t^2}{2!} + S_4 \frac{t^4}{4!} \dots, \tag{9}$$

where  $S_0, S_2$ , and  $S_4$  are the zeroth-, second- and fourth-order sum rules of the stress auto-correlation function, respectively. The expressions for  $S_0, S_2$  and  $S_4$  have already been given in the work of Tankeshwar *et al* [7]. For the sake of completeness and to correct a few typographic mistakes, these are given in the appendix. Defining the Fourier–Laplace transform of  $S(t)$  as

$$\tilde{S}(\omega) = i \int_0^\infty \exp(-i\omega t) S(t) dt, \tag{10}$$

we obtain from equations (8) and (10)

$$\tilde{S}(\omega) = - \frac{S(t=0)}{\omega + \tilde{M}(\omega)}. \tag{11}$$

Using equation (1) or (6) and (11), we obtain

$$\eta = \frac{i}{Vk_B T} \frac{S_0}{\tilde{M}(0)}. \tag{12}$$

Thus, the problem of calculating  $S(t)$  is now reduced to the evaluation of the memory function. Though there exists a microscopic expression for the memory function in terms of the projection operator, its calculation based on the mode coupling approach for any density and temperature is much more involved. In the present work, we use a phenomenological form for the memory function proposed earlier [8] which is given as

$$M(t) = M(0) \operatorname{sech}(t/\tau). \quad (13)$$

This memory function behaves as Gaussian at small times and as a simple exponential at long times. The parameters  $M(0)$  and  $\tau$  are so determined that short-time properties are exactly satisfied. It is found that

$$M(0) = \delta_1 = \frac{S_2}{S_0}, \quad (14)$$

and

$$\tau^{-2} = \delta_2 = \frac{S_4}{S_2} - \frac{S_2}{S_0}. \quad (15)$$

The memory function given by equation (13) is a solution of a nonlinear equation given as

$$\frac{d^2 M(t)}{dt^2} - \frac{M(t)}{\tau^2} + \frac{2M^3(t)}{\tau^2 M^2(0)} = 0. \quad (16)$$

The above equation is derivable from Mori's equation of motion by employing two approximations [16, 17] for the higher-order memory function. Equations (12)–(15) provide an expression for the viscosity given as

$$\eta = \frac{2n}{\pi k_B T} \left( \frac{S_0^2}{S_2} \right) \left( \frac{S_4}{S_2} - \frac{S_2}{S_0} \right)^{1/2}, \quad (17)$$

where  $n$  is the number density. We will use this equation to calculate  $\eta_B$  and  $\eta_1$ . This expression has already been used [18] to study the shear viscosity of expanded Rb using the corresponding sum rules.

### 3. Results and discussion

We have obtained numerical results for the zeroth-, second- and fourth-order sum rules of the bulk and LSAC functions from the expression given in the appendix for six thermodynamic states along the liquid–vapour co-existence curve of expanded rubidium. For the interaction potential, we have used the Ashcroft pseudo-potential with Ichimaru–Utsumi screening and the corresponding  $g(r)$  obtained through molecular dynamics (MD) simulation performed by Kahl and Kambayashi [14]. This potential has been used earlier [18] to study the shear viscosity of expanded Rb and has provided good agreement with computer simulation/experimental results. For the static triplet correlation function we have used a superposition approximation. The superposition approximation has been tested [19] to evaluate sum rules of transverse stress auto-correlation by comparing the results with those obtained by performing MD simulations for LJ fluids. It is found that, at the triple point, this approximation overestimates the results of the triplet contribution only by about 10%.

The thermodynamic states chosen in the present work, the values of  $\epsilon$  (the well depth of the potential) and  $\sigma$  (the position of the first zero of the potential) are given in table 1. The numerical integration involved in the evaluation of the sum rules are carried out by using the Gauss-quadrature method. The results obtained for the sum rules of LSAC and BSAC functions are, respectively, given in tables 2 and 3. In these tables and in what follows,  $S_{nm}$  represents the  $m$ -body contribution to the  $n$ th sum rule. It can be seen from the table that the

**Table 1.** Temperature,  $T$  (K), and mass density,  $\rho$  ( $\text{g cm}^{-3}$ ), of six thermodynamic states of Rb investigated in the present study.  $\sigma$  ( $\text{\AA}$ ) and  $\epsilon$  ( $10^{-12}$  ergs) are the position of the first zero and well depth of the potential.

State	$T$	$\rho$	$\sigma$	$\epsilon$
1	350	1.460	4.197 862	0.075 198 52
2	373	1.440	4.196 282	0.075 672 48
3	1073	1.130	4.107 260	0.087 710 05
4	1373	0.980	4.041 256	0.098 709 86
5	1673	0.830	3.950 153	0.116 712 9
6	1873	0.640	3.765 076	0.161 359 0

**Table 2.** Values of the sum rules of the LSAC functions.  $S_{nm}^1$  represents the  $m$ -body contribution to the  $n$ th-order sum rule.  $S_0$ ,  $S_2$  and  $S_4$  are in units of  $\epsilon^2$ ,  $\epsilon^3/m\sigma^2$  and  $\epsilon^4/m^2\sigma^4$ , respectively.

State	$S_0^1$	$S_{22}^1$	$S_{23}^1$	$S_{42}^1 \times 10^{-3}$	$S_{43}^1 \times 10^{-3}$
1	28.285	4191.5	-2991.1	985.290	-286.620
2	29.032	4366.6	-2938.0	1060.400	-276.820
3	47.553	6873.4	-2566.5	2626.200	-119.170
4	49.258	7057.4	-2181.7	2724.100	-101.600
5	39.507	3817.5	-1002.4	1366.900	-31.294
6	21.980	1726.8	-352.50	393.750	-8.099

**Table 3.** Values of the sum rules of the BSAC functions.  $S_{nm}^B$  represents the  $m$ -body contribution to the  $n$ th-order sum rule.  $S_0$ ,  $S_2$  and  $S_4$  are in units of  $\epsilon^2$ ,  $\epsilon^3/m\sigma^2$  and  $\epsilon^4/m^2\sigma^4$ , respectively.

State	$S_0^B$	$S_{22}^B$	$S_{23}^B$	$S_{42}^B \times 10^{-3}$	$S_{43}^B \times 10^{-3}$
1	15.936	2149.1	-1657.5	448.430	-44.222
2	16.297	2230.0	-1617.8	478.260	-35.668
3	25.141	3081.3	-1547.2	913.290	-43.859
4	26.667	3115.5	-1341.6	878.450	-110.540
5	19.910	1566.3	-643.4	401.220	-38.917
6	11.298	739.5	-220.2	112.310	-16.540

three-body contribution to the second sum rule varies from about 20 to 70% as we go from the sixth to the first thermodynamic state. On the other hand, the three-body contribution to the fourth sum rule varies only from about 2 to 30%. It implies that the time evolution of the stress auto-correlation function is strongly dependent on the triplet correlation's contribution, even at short times. The triplet contribution up to  $t^4$  terms in the expansion (9) is exactly taken care of by the theory involved. At longer times, higher-body contributions will also play their role which are incorporated in the present work only in an approximate manner. Here, it is also interesting to note that the maximum three-body contribution is about 50% in the case of LJ fluids at the triple point. Thus, a greater contribution of the multiparticle correlation in liquid metals as compared to inert fluids may be attributed to the softness of the potential as sum rules are found to be more sensitive to the details of the potential at smaller distances.

The longitudinal and bulk viscosity of the expanded rubidium is calculated from equation (17) by using the values of the sum rules from tables 2 and 3. The results obtained for the bulk and longitudinal viscosity of expanded Rb are given in table 4. In table 4 we have also presented results for the shear viscosity obtained in an exactly similar fashion and are compared with experimental results (column 3) taken from [14]. The results obtained for  $\eta_B$

**Table 4.** Shear, longitudinal and bulk viscosities, in centipoise, for six thermodynamic states of Rb. The subscript 2 represents the fact that viscosities have been calculated by including only two-body correlations.

State	$\eta_s$	$\eta_s(\text{exp})$	$\eta_{s2}$	$\eta_l$	$\eta_{l2}$	$\eta_B$	$\eta_{B2}$	$\eta_l - \frac{4}{3}\eta_s$	$\eta_B/\eta_s$	$\eta_B/\eta_s$ [15]
1	0.484	0.476	0.089	2.465	0.247	2.020	0.141	1.811	4.12	1.59
2	0.412	0.433	0.087	1.932	0.240	1.475	0.136	1.378	3.55	1.57
3	0.136	0.136	0.083	0.517	0.219	0.402	0.117	0.331	2.94	1.35
4	0.094	0.112	0.065	0.365	0.184	0.264	0.101	0.239	2.77	1.26
5	0.103	0.9996	0.078	0.338	0.198	0.240	0.101	0.200	2.31	1.11
6	0.056	0.0870	0.044	0.168	0.109	0.093	0.051	0.091	1.61	1.00

from  $\eta_l - 4/3\eta_s$  are also depicted in table 4. The closeness of the results from  $\eta_l - (4/3)\eta_s$  with those calculated directly for  $\eta_B$  demonstrates that the memory function for longitudinal, transverse and bulk stress auto-correlation functions can have the same functional form but with different relaxation times. The calculations [15], which use the same relaxation time for BSAC as that for the shear viscosity, result in a ratio of  $\eta_B/\eta_s$  given in the last column of table 4. It can also be seen from the table that our present values of  $\eta_B/\eta_s$  vary from 4.12 to 1.61. The experimental value [11] of  $\eta_B/\eta_s$  at a thermodynamic state which is close to the first thermodynamic state is 3.73. Thus, we see that the prediction of our values of bulk viscosity is quite reasonable. The higher value of this ratio at  $T = 373$  K is not an unexpected result, as can be judged from the available experimental value [11] of 2.4 for liquid Na and K. Here, it may be noted that the maximum value of this ratio for LJ fluids at the triple point is around 0.6.

In order to study the importance of the multiparticle contribution to viscosity, we have calculated  $\eta_s$ ,  $\eta_B$  and  $\eta_l$  by neglecting three-body contributions to the second and fourth sum rules. The results obtained are given in table 4 and are represented by  $\eta_{s2}$ ,  $\eta_{B2}$  and  $\eta_{l2}$ . It can be seen that the three-body correlations play a significant role in determining the viscosity of the system and the effect of three-body correlations increases as one moves towards the melting point.

#### 4. Summary and conclusion

In this paper, we have given estimates of the bulk and longitudinal viscosities of expanded Rb for six thermodynamic states. The values of the bulk and longitudinal viscosities have been contrasted with the corresponding values of shear viscosity. The ratio of bulk to shear viscosity has been compared with the experimental result available only at a density close to the melting point. It is found that the ratio of bulk viscosity to shear viscosity decreases from 4.12 to 1.61 on moving from  $T = 373$  to 1873 K along the liquid–vapour co-existence curve. We have used the Mori memory function formalism and values of the first three non-vanishing sum rules. The sum rules have been evaluated using a density-dependent potential and corresponding  $g(r)$  obtained through simulation studies. It has also been found that three-body correlation functions play a very important role in determining the viscosity of the liquid metal.

#### Appendix. Expressions for sum rules

The expression for the zeroth sum rule of the LSAC function,  $S_0^l$ , is obtained by putting  $t = 0$  in equation (2). The expression thus obtained after taking ideal values of  $VdP/dE$ ,  $PV$  and

$\bar{E}$  is given as

$$S_0^1 = \frac{4}{3}(k_B T)^2 + \frac{2\pi n}{15} k_B T \int_0^\infty dr r^4 g(r)(3Ar^2 + 5B). \quad (A.1)$$

The expression for  $S_2^1$  is obtained by evaluating the thermodynamic average

$$S_2^1 = \langle \dot{J}^{xx}(t) \dot{J}^{xx}(t) \rangle_{t=0}, \quad (A.2)$$

where  $\dot{J}^{xx}(t)$  is the first time derivative of  $J^{xx}(t)$ . The final expression for  $S_2^1$  involving only a static pair and triplet correlation function is given as

$$\begin{aligned} S_2^1 = & \frac{4\pi k_B T n}{15m} \int_0^\infty r^2 g(r) dr [r^2(5B^2 + 3A^2 r^4 + 6ABr^2) + k_B T(18Cr^4 + 165Ar^2 + 225B)] \\ & + \frac{8\pi^2 k_B T n^2}{15m^2} \int_0^\infty r^2 dr \int_0^\infty r_1^2 dr_1 \int_{-1}^1 d\beta_1 g_3(\mathbf{r}, \mathbf{r}_1) \\ & \times \beta_1 [r r_1 (Ar^2 + B)(A_1 r_1^2 + 5B_1) + 2\beta_1^2 A A_1 r^3 r_1^3]. \end{aligned} \quad (A.3)$$

In the above expressions and in what follows,  $g(r)$  and  $g_3(\mathbf{r}, \mathbf{r}_1)$  are the static pair and triplet correlation functions and

$$\begin{aligned} B &= \frac{1}{r} \frac{dU(r)}{dr}, & A &= \frac{1}{r} \frac{dB}{dr}, \\ C &= \frac{1}{r} \frac{dA}{dr}, & D &= \frac{1}{r} \frac{dA}{dr}. \end{aligned} \quad (A.4)$$

The subscript 1 on these implies that the argument of the potential  $U(r)$  is replaced by  $r_1$ . The fourth sum rule of the LSAC is defined as

$$S_4^1 = \langle \ddot{J}^{xx}(t) \ddot{J}^{xx}(t) \rangle_{t=0}, \quad (A.5)$$

where  $\ddot{J}^{xx}(t)$  is the second time derivative of  $J^{xx}(t)$ . The final expression for  $S_4^1$  involves static pair, triplet and quadruplet contributions and is given as

$$\begin{aligned} S_4^1 = & \frac{4\pi n}{15} \frac{k_B T}{m} \int_0^\infty dr g(r) r^2 [54(k_B T)^2 (Dr^4 + 10Cr^2 + 15A) + k_B T(1890B^2 \\ & + 1504A^2 r^4 + 2340ABr^2 + 216BCr^4 + 324ACr^6 + 18C^2 r^8) \\ & + 2r^2(5B^3 + 9AB^2 r^2 + 9A^2 Br^4 + 3A^3 r^6)] \\ & + 8\pi^2 n^2 \frac{(k_B T)}{15m^2} \int_0^\infty dr \int_0^\infty dr_1 \int_{-1}^1 d\beta_1 g_3(\mathbf{r}, \mathbf{r}_1) r^2 r_1^2 [k_B T(105(9BB_1 \\ & + 3BA_1 r_1^2 + \frac{1}{3}AA_1 r^2 r_1^2(6\beta_1^2 + 1) + 3AB_1 r^2) + 30(3B_1 Cr^4 + 15AB_1 r^2 \\ & + 3A_1 Cr^4 r_1^2 \beta_1^2 + AA_1 r^2 r_1^2(9\beta_1^2 + 2)) + 12rr_1 \beta_1(3B_1 Cr^2 + 15AB_1 \\ & + CA_1 r^2 r_1^2(2\beta_1^2 + 1) + 11AA_1 r_1^2) + 3(CC_1 r^4 r_1^4 \beta_1^2(2\beta_1^2 + 1) \\ & + 2A_1 Cr^4 r_1^2(8\beta_1^2 + 1) + AA_1 r^2 r_1^2(28\beta_1^2 + 9))) + r(r + 4\beta_1 r_1)(3AA_1 B_1 r^2 r_1^2 \\ & + 6ABB_1 r^2 + 5B^2 B_1) + rA_1 B^2(12r_1^3 \beta_1 + rr_1^2(2\beta_1^2 + 1)) + A_1 A^2 r^5 r_1^2 \beta_1(3\beta_1 r \\ & + 4r_1(2\beta_1^2 + 1)) + 4Ar^3 A_1 r_1 \beta_1 B(3\beta_1 r + 4r_1(2\beta_1^2 + 1)) - (1/2)[5r^2 B B_1 B_2 \\ & + BA_1 B_2 r_1^2(3r_1^2 + r^2(2\beta_1^2 + 1)) + 3\beta_1^2 r^4 A_1 AB_2 r_1^2 + BA_1 A_2 r_1^2 r_2 \beta_3 \\ & \times ((3\beta_1 r^3 - 3r_1^3) - rr_1 r_2(\beta_2 + 2\beta_1 \beta_3) - 6r_1^2 r_2 \beta_3) \\ & + \beta_1 \beta_2 r^4 AA_1 A_2 r_1^2 r_2^2(5\beta_3 - 2\beta_1 \beta_2) + BB_1 A_2 r^2(3\beta_2^2 r_2^2 + r_1^2(1 - \beta_1^2))] \\ & + \left( \frac{\pi n}{15} k_B T \int_0^\infty dr r^4 g(r)(3Ar^2 + 5B) \right) \left( \frac{4\pi n}{3} \int_0^\infty dr r^2 g(r)(Ar^2 + 3B) \right)^2. \end{aligned} \quad (A.6)$$



The last term in equation (A.6) represents the approximate four-body contribution in terms of the static pair correlation function. In the above equation  $\mathbf{r}_2 = \mathbf{r}_1 - \mathbf{r}$  and subscript 2 with  $A$ ,  $B$  and  $C$  imply that the argument of  $U(r)$  is changed from  $r$  to  $r_2$ . Further,  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  are cosines of the angles between  $\mathbf{r}$  and  $\mathbf{r}_1$ ,  $\mathbf{r}$  and  $\mathbf{r}_2$  and  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , respectively.

Expressions for the sum rules of the bulk stress auto-correlation function can also be obtained in a similar fashion. The expression for the zeroth sum rule of the bulk stress auto-correlation function after taking ideal values of  $VdP/dE$ ,  $PV$  and  $\bar{E}$  are obtained as

$$S_0^B = \frac{2\pi n}{9} k_B T \int_0^\infty dr r^4 g(r) (Ar^2 - B). \quad (\text{A.7})$$

The expression for the second sum rule is

$$\begin{aligned} S_2^B = & \frac{4\pi n}{9m} (k_B T)^2 \int_0^\infty dr r^2 g(r) [(6Cr^4 + 45Ar^2 + 45B) + r^2 (k_B T)^{-1} (Ar^2 + B)^2] \\ & + 8\pi^2 n^2 \frac{(k_B T)}{9m^2} \int_0^\infty dr \int_0^\infty dr_1 \int_{-1}^1 d\beta_1 g_3(\mathbf{r}, \mathbf{r}_1) r^2 r_1^2 r r_1 \beta_1 \\ & \times (AA_1 r^2 r_1^2 + BA_1 r_1^2 + AB_1 r^2 + BB_1). \end{aligned} \quad (\text{A.8})$$

The expression for the fourth sum rule of the bulk stress auto-correlation function is given as

$$\begin{aligned} S_4^B = & \frac{4\pi n}{9} \left( \frac{k_B T}{m} \right)^2 \int_0^\infty dr g(r) r^2 [18(k_B T)^2 (Dr^4 + 10Cr^2 + 15A) + k_B T (378B^2 + 432A^2 r^4 \\ & + 612ABr^2 + 72BCr^4 + 108ACr^6 + 6C^2r^8) + 2r^2 (B + Ar^2)^3 - 4B^3 r^2] \\ & + 8\pi^2 n^2 \frac{(k_B T)^2}{9m^2} \int_0^\infty dr \int_0^\infty dr_1 \int_{-1}^1 d\beta_1 g_3(\mathbf{r}, \mathbf{r}_1) r^2 r_1^2 [63(3BB_1 + BA_1 r_1^2 \\ & + AA_1 r^2 r_1^2 \beta_1^2 + AB_1 r^2) + 18(B_1 Cr^4 + 5AB_1 r^2 + A_1 Cr^4 r_1^2 \beta_1^2 + AA_1 r^2 r_1^2 \\ & \times (2\beta_1^2 + 1)) + 8rr_1 \beta_1 (B_1 Cr^2 + 5AB_1 + CA_1 r^2 r_1^2 + 5AA_1 r_1^2) \\ & + 3r^2 r_1^2 (CC_1 r^2 r_1^2 \beta_1^2 + A_1 Cr^2 (2\beta_1^2 + 1) + AC_1 r_1^2 (2\beta_1^2 + 1) + AA_1 (4\beta_1^2 + 7)) \\ & + k_B T^{-1} [4rr_1 \beta_1 (2AA_1 Br^2 r_1^2 + AB B_1 r^2 + B^2 B_1 + A_1 B^2 r_1^2 + A^2 A_1 r^4 r_1^2 \\ & + BAB_1 r_2 + A^2 B_1 r^4) + r^2 (Ar^2 + B)^2 (A_1 r_1^2 \beta_1^2 + B_1) \\ & - \frac{1}{2} [r^2 B B_1 B_2 + BA_1 B_2 r_1^2 r^2 \beta_1^2 + \beta_1^2 r^4 A_1 A B_2 r_1^2 + BA_1 A_2 r_1^2 r_2^2 r^2 \beta_3 \beta_1 \beta_2 \\ & + \beta_1 \beta_2 r^4 AA_1 A_2 r_1^2 r_2^2 (2\beta_3 - \beta_1 \beta_2) + BB_1 A_2 r^2 \beta_2^2 r_2^2 \\ & + AB_1 B_2 r^4 + AB_1 A_2 r^4 r_2^2 \beta_2^2]]. \end{aligned} \quad (\text{A.9})$$

These expressions are suitable for numerical integration.

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